

TRANSLATION

[19]



Europäisches Patentamt
European Patent Office
Office européen des brevets

[11] Publication number:
EP 0,831,116 A1

[12]

EUROPEAN PATENT APPLICATION

[43] Date of publication of the application:
March 25, 1998 Bulletin 1998/13

[51] Int. Cl.⁶: C08K 3/04, C08L 59/00

[21] Application number: 9711579.9

[22] Date of filing: September 11, 1997

[84] DESIGNATED CONTRACTING STATES:
AT, BE, CH, DE, DK, ES, FI, FR, GB,
GR, IE, IT, LI, LU, MC, NL, PT, SE

[30] PRIORITY:
SEPTEMBER 18, 1996
DE 19638036 (GERMANY)

[71] APPLICANT:
BASF
AKTIENGESELLSCHAFT
67056 LUDWIGSHAFEN,
GERMANY (DE)

[72] INVENTORS:

• PLACHETTA, CHRISTOPH,
PH.D.

67117
LIMBURGEHOF
GERMANY (DE)

• HENNIG, INGOLF, PH.D.
68809

NEULUSSHEIM
GERMANY (DE)

• KELLER, BRUNO
55263
WACKERNHEIM
GERMANY (DE)

EP 0,831,116 A1

[54] ELECTROSTATICALLY COATABLE MOLDED PARTS

[57] THE USE OF THERMOPLASTIC MOLDING
COMPOUNDS MADE OF

- A) 30% TO 94% BY WEIGHT OF A
POLYOXYMETHYLENE HOMOPOLYMER OR
POLYOXYMETHYLENE COPOLYMER,
- B) 6% TO 10% BY WEIGHT OF CARBON BLACK
WITH A PORE VOLUME (DBP ADSORPTION)
ACCORDING TO DIN 53 601 OF AT LEAST 350
ML/100 GRAMS
- C) 0% TO 2% BY WEIGHT OF AN ALKALI OR
EARTH ALKALI COMPOUND OR MIXTURES
THEREOF
- D) 0% TO 2% BY WEIGHT OF A POLYAMIDE
- E) 0% TO 60% BY WEIGHT OF FURTHER
ADDITIVES AND PROCESSING AUXILIARIES,

WHEREBY THE PERCENTAGES BY WEIGHT OF
COMPONENTS A) THROUGH E) ADD UP TO 100%,
FOR THE PRODUCTION OF ELECTROSTATICALLY
COATABLE MOLDED PARTS.

Description

The invention relates to the use of thermoplastic molding compounds made of

- A) 30% to 94% by weight of a polyoxymethylene homopolymer or polyoxymethylene copolymer,
- B) 6% to 10% by weight of carbon black with a pore volume (DBP adsorption) according to DIN 53 601 of at least 350 ml/100 grams
- C) 0% to 2% by weight of an alkali or earth alkali compound or mixtures thereof
- D) 0% to 2% by weight of a polyamide
- E) 0% to 60% by weight of further additives and processing auxiliaries,

whereby the percentages by weight of components A) through E) add up to 100%, for the production of electrostatically coatable molded parts.

Moreover, the invention relates to the electrostatically coatable molded parts that can be obtained in this manner.

POM molding compounds containing carbon black are known, among others, from EP-A 327 384, DE-A 40 07 766, EP-A 247 765 and EP 327 384.

Furthermore, commercially available products such as Ultraform® N2520 L (registered trademark of Ultraform GmbH) and Hostaform® C 9021 ELS (registered trademark of Hoechst AG) are provided with conventional conductive carbon black or color black,

which are well-suited for imparting an antistatic finishing or for dissipating static electricity.

The use of such molded parts is described, for example, in general works such as those by H.J. Mair, *Elektrisch leitende Kunststoffe* [Electrically conductive plastics], published by Hanser Verlag, 1989, pp. 1 to 18 or by R.G. Gilg, *Ruß für leitfähige Kunststoffe* [Carbon black for conductive plastics], published in *Kunststoffberater* 22, p. 262 (1977) and 22, p. 312 (1977), by S. Roth, H.J. Mair, *Elektrisch leitende Kunststoffe* [Electrically conductive plastics], published by GAK, Volume 48 (Issue 9), pp. 634-639 (1995).

The above-mentioned literature consistently considers it to be a disadvantage that carbon black in large quantities has a negative influence on the mechanical properties of POM, since carbon black is an acidic additive and damages the POM matrix.

Until now, the worse mechanical properties were compensated for by adding an impact strength modifier such as thermoplastic polyurethanes (TPU). However, the carbon black accumulates, particularly in the elastomer phase, so that the volume resistance needed for electrostatic coating is not achieved. Furthermore, in the products that are known from the state of the art or that are commercially available, the conductivity is not sufficient – or else the volume resistance is not low enough – to be able to coat these products electrostatically. According to C. Koevoets, D. Noordegraaf, U. Hofmann, *Kunststoffe* [Plastics] 86 (1996) 3, pp. 358-360, volume resistivity values of less than 10^5 Ohm/cm are needed in order to be able to carry out an electrostatic coating without any problems.

Furthermore, EP-A 363 103 discloses that POM molding compounds can only be electrostatically coated after a complicated chemical or physical pretreatment. Electrostatically coatable parts are needed for applications in the automotive industry for reasons of design and surface protection.

Therefore, the objective of the present invention was to provide molded parts made of polyoxymethylene that are electrostatically coatable and that, at the same time, have a good resistance to fuels and chemicals as well as a good stiffness, especially at elevated temperatures.

Accordingly, the above-defined use of POM molding compounds was discovered. Preferred embodiments can be found in the subordinate claims.

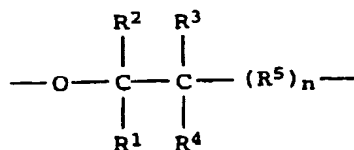
As component A), the molding compounds that can be used according to the invention contain 30% to 94% by weight, preferably 50% to 94% by weight and especially 60% to 90% by weight, of a polyoxymethylene homopolymer or polyoxymethylene copolymer.

Such polymers are known to the person skilled in the art and are described in the literature.

In general, these polymers have at least 50 mol-% of recurring units $-\text{CH}_2\text{O}-$ in the polymer main chain.

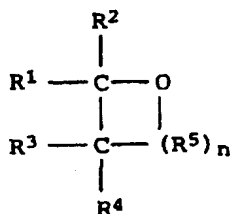
The homopolymers are generally made by means of polymerization of formaldehyde or trioxane, preferably in the presence of suitable catalysts.

Within the scope of the invention, polyoxymethylene copolymers are preferred as component A, especially those that, in addition to the recurring units $-\text{CH}_2\text{O}-$, have up to 50 mol-%, preferably 0.1 to 20 mol-%, and especially 0.3 to 10 mol-% of recurring units.



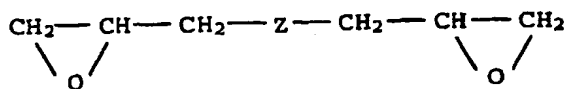
EP 0 831 116 A1

wherein R^1 to R^4 , independently of each other, stand for a hydrogen atom, a C_1 - C_4 -alkyl group or a halogen-substituted alkyl group having 1 to 4 carbon atoms and R^5 stands for a $-CH_2-$, $-CH_2O-$, a C_1 - C_4 -alkyl or C_1 - C_4 -haloalkyl-substituted methylene group or for a corresponding oxymethylene group and n has a value in the range from 0 to 3. Advantageously, these groups can be introduced into the copolymer by means of the ring-opening of cyclic ethers. Preferred cyclic ethers are those having the formula

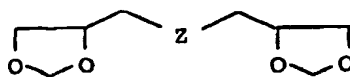


wherein R^1 to R^5 and n have the meanings given above. Only by way of example, mention is made of ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, 1,3-butylene oxide, 1,3-dioxane, 1,3-dioxolane and 1,3-dioxepane as cyclic ethers as well as of linear oligoformals or polyformals such as polydioxolane or polydioxepane as comonomers.

Likewise suitable as component A) are oxymethylene terpolymers are that are produced by reacting trioxane, one of the above-mentioned cyclic ethers with a third monomer, preferably bifunctional compounds having the formula



and/or



wherein Z stands for a chemical compound, for $-O-$, $-ORO-$ ($R = C_1-C_8$ -alkylene or C_2-C_8 -cycloalkylene).

Preferred monomers of this type are ethylene diglycide, diglycidyl ether and diether from glycidyls and formaldehyde, dioxane or trioxane in a molar ratio of 2 : 1 as well as diethers from 2 moles of glycidyl compounds and 1 mol of an aliphatic diol having 2 to 8 carbon atoms such as, for example, the diglycidylether of ethylene glycol, 1,4-butane diol, 1,3-butane diol, cyclobutane-1,3-diol, 1,2-propane diol and cyclohexane-1,4-diol, to name just a few examples.

Methods for the production of the above-mentioned homopolymers and copolymers are known to the person skilled in the art and described in the literature so that there is no need to elaborate on this here.

The preferred polyoxymethylene copolymers have melting points of at least 150°C [302°F] and molecular weights (weight average value M_w) in the range from 5,000 to 200,000, preferably from 7,000 to 150,000.

Terminal group-stabilized polyoxymethylene polymers that have C-C bonds at the ends of the chains are especially preferred.

As component A), it is especially possible to use products that still contain a relatively high proportion (generally $> 0.1\%$ by weight) of thermally unstable fractions. Components C) and D) – especially if they were pre-mixed with the polyoxymethylene prior to the mixing – stabilize such raw polyoxymethylenes very well.

As component B), the molding compounds that can be used according to the invention contain 6% to 10% by weight, preferably 6% to 8% by weight and especially preferably

EP 0 831 116 A1

6% to 7% by weight, of carbon black with a pore volume (DBP dibutyl phthalate adsorption) according to DIN 53 601 of at least 350 ml/100 grams, preferably at least 370 ml/100 grams.

The DBP adsorption rate is generally determined according to DIN 53 601 or ASTM-D 2414 and it constitutes an indicator of the structure of the carbon black in question. The term structure refers to the linking of carbon black primary particles to form aggregates. In order to determine this characteristic value, dibutyl phthalate is dripped into 10 grams of pigment carbon black that was placed into a kneader with measurable force transmission (plastograph) until the maximum torque (cross-linking point of the carbon black) has been exceeded.

Preferably, component B) has a specific surface area according to BET (according to DIN 60 132 or ASTM-D 3037) of at least 900 m²/g, preferably 950 m²/g and a iodine adsorption (according to DIN 53 582 or ASTM-D 1510) of at least 950 m²/g, preferably 1000 m²/g and especially 1050 m²/g.

The mean primary particle size is normally 10 nm to 50 nm, preferably 25 nm to 35 nm.

Such types of carbon black are available, for example, under the trademarks Printex® XE2 (Degussa AG) or Ketjen Black EC DJ 600 (Akzo).

As component C), the molding compounds that can be used according to the invention contain – relative to the total weight of components A) through E) – 0% to 2% by weight, preferably 0.001% to 1.5% by weight, and especially 0.1% to 1% by weight, of an alkali and/or earth alkali compound.

In general, all earth alkali metal cations and/or alkali metal cations can be used, whereby lithium, sodium, potassium and calcium cations are preferred.

Alkali and/or earth alkali compounds should be understood according to the invention to mean those organic or inorganic salts that undergo an alkaline reaction in aqueous solutions or suspensions.

As inorganic salts, mention should be made, for example, of carbonates, hydrogen carbonates, hydroxides, oxides or phosphates, whereby alkali carbonates such as potassium carbonate and sodium carbonate are especially preferred.

Organic salts are, for example, alcoholates of C₂-C₁₂-alcohols, phenolates or salts of carboxylic acids having 2 to 12 carbon atoms, whereby citrates, oxalates or tartrates are especially preferred.

Special preference is given to alkali hydroxides, especially potassium hydroxide and sodium hydroxide which are preferably added in the form of a 10% to 70% aqueous solution, preferably a 40% to 60% aqueous solution, during the production of the POM molding compounds, whereby the metering can be carried out together with the carbon black B).

The polyamides that can be used as component D) are generally known. Semi-crystalline or amorphous resins such as those described, for example, in the Encyclopedia of Polymer Science and Engineering, Vol. 11, pp. 315 to 489, John Wiley & Sons, Inc. 1988, can be used, whereby the melting point of the polyamide is preferably below 225°C [437°F], and especially preferably below 215°C [419°F].

Examples of this are polyhexamethylene azelaic acid amide, polyhexamethylene sebacic acid amide, polyhexamethylene dodecanoic diacid amide, poly-11 amino undecanoic acid amide and bis-(p-aminocyclohexyl)-methane dodecanoic acid diamide or the products obtained by means of the ring-opening of lactase, for example, or polylaurinlactam. Poly-

amides on the basis of terephthalic acid or isophthalic acid as the acid component and/or trimethyl hexamethylene diamine or bis-(p-aminocyclohexyl)-propane as the diamine component as well as polyamide basic resins that have been produced by means of the copolymerization of two or more of the above-mentioned polymers or their components are also suitable.

As especially suitable polyamides, mention should be made of mixed polyamides on the basis of caprolactam, hexamethylene diamine, p,p'-diamino dicyclohexyl methane and adipic acid. An example of this is the product sold under the name Ultramid® 1 C by BASF Aktiengesellschaft.

Other suitable polyamides are sold by the DuPont Company under the name Elvamide®.

The production of these polyamides is likewise described in the above-mentioned publication. The ratio of terminal amino groups to terminal acid groups can be regulated by varying the molar ratio of the starting compounds.

The proportion of the polyamide in the molding compound according to the invention is 0% to 2% by weight, preferably 0.005% to 1.8% by weight, especially preferred 0.04% to 1.6% by weight.

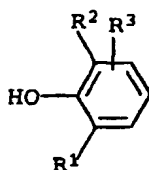
As component E), the molding compounds that can be used according to the invention can contain up to 60% by weight, preferably up to 50% by weight, of conventional additives or processing auxiliaries.

As the nucleation agents, according to a preferred embodiment, the molding compounds can contain a melamine formaldehyde condensate. Suitable produces are described, for example, in DE-A 25 40 207.

EP 0 831 116 A1

As a matter of principle, suitable sterically hindered phenols (antioxidants) comprise all compounds with a phenolic structure that have at least one sterically complex group on the phenolic ring.

Preferably, for example, compounds having the formula



are possibilities, wherein

R^1 and R^2 stand for an alkyl group, a substituted alkyl group or a substituted triazole group, whereby the radicals R^1 and R^2 can be the same or different and

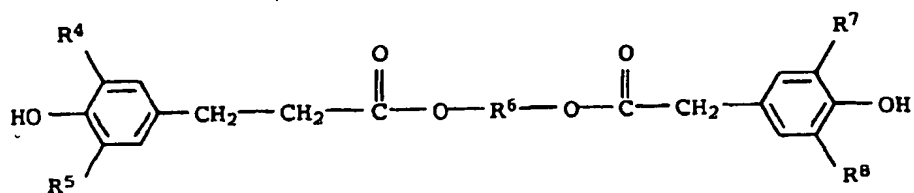
R^3 stands for an alkyl group, a substituted alkyl group, an alkoxy group or a substituted amino group.

Antioxidants of the above-mentioned type are described, for example, in DE-A 27 02 661 (U.S. Pat. No. 4,360,617).

Another group of preferred, sterically hindered phenols are derived from substituted benzene carboxylic acids, especially from substituted benzene propionic acids.

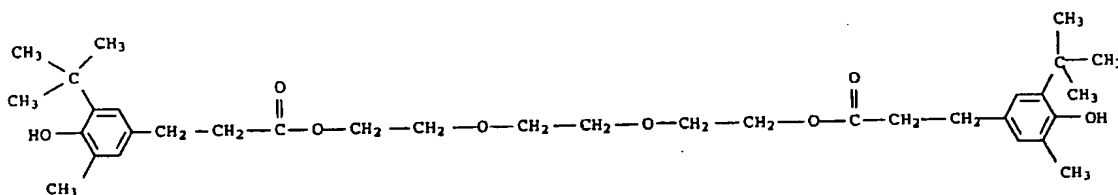
Especially preferred compounds from this class are compounds having the formula

EP 0 831 116 A1

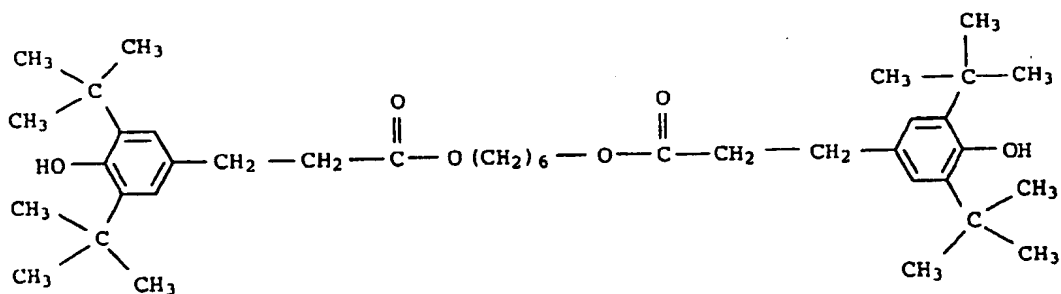


wherein R^4 , R^5 , R^7 and R^8 , independently of each other, stand for C_1 - C_8 -alkyl groups which, in turn, can be substituted (at least one of them is a sterically hindered complex group) and R^6 stands for a bivalent aliphatic radical having 1 to 10 carbon atoms, which can also have C-O bonds in the main chain.

Preferred compounds that have this formula are



(Irganox® 245 made by the Ciba-Geigy company)



(Irganox® 259 made by the Ciba-Geigy company)

By way of example, the following are mentioned as sterically hindered phenols:

2,2'-methylene-bis-(4-methyl-6-*tert.*-butylphenol), 1,6-hexane diol-bis-[3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)-propionate], pentaerythryl-tetrakis-[3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)-propionate], distaryl-3,5-di-*tert.*-butyl-4-hydroxy-benzylphosphonate, 2,6,7-trioxa-1-phosphabicyclo-[2.2.2]oct-4-yl-methyl-3,5-di-*tert.*-butyl-4-hydroxyhydrocinnamate, 3,5-di-*tert.*-butyl-4-hydroxyphenyl-3,5-distearyl-thiotriazylamine, 2-(2'-hydroxy-3'-hydroxy-3',5'-di-*tert.*-butylphenyl)-5-chlorobenzotriazole, 2,6-di-*tert.*-butyl-4-hydroxymethylphenol, 1,3,5-trimethyl-2,4,6-tris-(3,5-di-*tert.*-butyl-4-hydroxybenzyl)-benzene, 4,4'-methylene-bis-(2,6-di-*tert.*-butylphenol), 3,5-di-*tert.*-butyl-4-hydroxy-benzyl-dimethylamine and N,N'-hexamethylene-bis-3,5-di-*tert.*-butyl-4-hydroxyhydrocinnamide.

The following have proven to be especially effective and are consequently preferably used: 2,2'-methylene-bis-(4-methyl-6-*tert.*-butylphenyl), 1,6-hexane diol-bis-[3,5-di-*tert.*-butyl-4-hydroxyphenyl)-propionate (Irganox® 259), pentaerythrityl-tetrakis-[3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)-propionate] and the above-mentioned Irganox® 245 of the Ciba Geigy company, which is especially well-suited.

The antioxidants, which can be employed individually or as mixtures, can be used in an amount of 0.05% to 2% by weight, preferably from 0.1% to 1.0% by weight.

In many cases, sterically hindered phenols with not more than one sterically hindered group in the ortho position relative to phenolic hydroxy groups have proven to be especially advantageous, in particular, in evaluating the color stability during storage in diffuse light over prolonged periods of time.

By also using a polycondensation product from 2,2-di(4-hydroxyphenyl)propane (bisphenol A) and epichlorohydrine, in many cases the dispersability of the polyamides employed can be improved.

EP 0 831 116 A1

Such condensation products from epichlorohydrine and bisphenol A are commercially available. Methods for their production are likewise known to the person skilled in the art. Trademarks of these polycondensates are Phenoxy® (made by Union Carbide Corporation) or Epikote® (Shell company). The molecular weight of the polycondensates can vary over a wide range; in principle, all of the types that are commercially available are suitable.

Furthermore, as component E), 0.002% to 2.0% by weight, preferably 0.005% to 0.5% by weight and especially 0.01% to 0.3% by weight, of one or more earth alkali silicates and/or earth alkali glycerophosphates can be present. Preferably calcium and especially preferably magnesium have proven to be excellent as earth alkali metals for the formation of the silicates and glycerophosphates. It is advantageously possible to use magnesium glycerophosphate and/or calcium silicate and preferably magnesium silicate, whereby as the earth alkali silicates, special preference is given to those that are described by the formula



wherein

Me is an earth alkali metal, preferably calcium or especially magnesium,

x is a number from 1.4 to 10, preferably from 1.4 to 6 and

n is a number equal to or greater than 0, preferably 0 to 8.

These compounds E) are advantageously used in finely ground form. Products with an average particle size of less than 100 µm, preferably less than 50 µm, are especially well-suited.

As component E, the thermoplastic molding compounds according to the invention contain 0% to 50% by weight, preferably 0% to 45% by weight, of an impact modified polymer (often also referred to as a rubber-elastic polymer or elastomer).

Preferred types of such elastomers are the so-called ethylene propylene (EPM) or ethylene propylene diene (EPDM) rubbers.

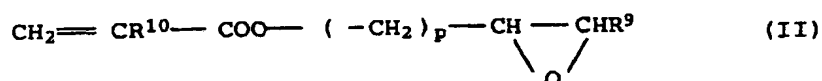
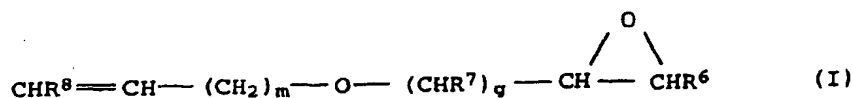
Generally speaking, EPM rubbers have practically no more double bonds whereas EPDM rubbers can have 1 to 20 double bonds per 100 carbon atoms.

As diene monomers for EPDM rubbers, mention should be made, for example, of conjugated dienes such as isoprene and butadiene, unconjugated dienes having 5 to 25 carbon atoms such as penta-1,4-diene, hexa-1,4-diene, hexa-1,5-diene, 2,5-dimethylhexa-1,5-diene and octa-1,4-diene, cyclic dienes such as cyclopentadiene, cyclohexadiene, cyclooctadiene and dicyclopentadiene as well as alkenylnorbornenes such as 5-ethylidene-2-norbornene, 5-butylidene-2-norbornene, 2-methyl-5-norbornene, 2-isopropenyl-5-norbornene and tricyclobienes such as 3-methyl-tricyclo(5.2.1.0.2.6)-3,8-decadiene or mixtures thereof. Preference is given to hexa-1,5-diene-5-ethylidene-norbornene and dicyclopentadiene. The diene content of the EPDM rubbers is preferably 0.5% to 50% by weight, especially 1% to 8% by weight, relative to the total weight of the rubber.

The EPDM rubbers can also be grafted with additional monomers, for example, with glycidyl(meth)acrylates, (meth)acrylic acid esters and (meth)acrylamides.

Another group of preferred rubbers includes copolymers of ethylene with esters of (meth)acrylic acid. In addition, the rubbers can also comprise monomers containing epoxy groups. These monomers containing epoxy groups are preferably incorporated into

the rubber by adding monomers containing epoxy groups and having the general formulas I and II to the monomer mixture



wherein R^6 to R^{10} stand for hydrogen or alkyl groups having 1 to 6 carbon atoms and m is an integer ranging from 0 to 20, g is an integer ranging from 0 to 10, and p is an integer ranging from 0 to 5.

Preferably, the radicals R^6 to R^8 stand for hydrogen, whereby m stands for 0 or 1 and g stands for 1. The corresponding compounds are allylglycidyl ether and vinylglycidyl ether.

Preferred compounds having Formula II are esters of acrylic acid and/or methacrylic acid, which contain epoxy groups, such as glycidylacrylate and glycidylmethacrylate.

Advantageously, the copolymers consist of 50% to 98% by weight of ethylene, 0% to 20% by weight of monomers containing epoxy groups and of the remaining amount of (meth)acrylic acid esters.

Special preference is given to copolymers made of

50% to 98% by weight, especially 55% to 95% by weight, of ethylene,
especially 0.3% to 20% by weight, of glycidylacrylate

EP 0 831 116 A1

and/or

0% to 40% by weight, especially 0.1% to 20% by weight, of glycidyl methacrylate
and

1% to 50% by weight, especially 10% to 40% by weight, of n-butylacrylate
and/or 2-ethyl hexylacrylate.

Additional preferred esters of acrylic and/or methacrylic acids are methylester, ethylester, propylester and i-butylester or t-butylester.

In addition, vinyl esters and vinyl ethers can also be used as comonomers.

The ethylene copolymers described above can be produced by means of known methods, preferably by means of statistical copolymerization under high pressure and elevated temperature. Such methods are generally known.

Preferred elastomers are also emulsion polymers, whose production is described, for example, in Blackley in the monograph titled "Emulsion Polymerization". The usable emulsifiers and catalysts are generally known.

Fundamentally, homogeneously structured elastomers or those with a shell structure can be used. The shell-like structure is determined by the sequence of the addition of the individual monomers; the morphology of the polymers is also influenced by this sequence of addition.

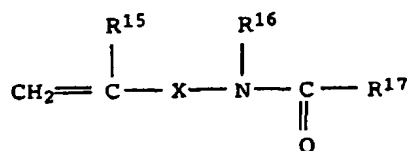
Only by way of an example, as monomers for the production of the rubber part of the elastomer, mention is made of acrylates such as, for example, n-butylacrylate and 2-ethylhexylacrylate, corresponding methacrylates, butadiene and isoprene as well as

mixtures thereof. These monomers can be copolymerized with additional monomers such as, for example, styrene, acrylonitrile, vinyl ethers and additional acrylates or methacrylates such as methyl methacrylate, methylacrylate, ethylacrylate and propylacrylate.

The soft or rubber phase (with a glass transition temperature of less than 0°C [32°F]) of the elastomers can constitute the core, the outer shell or a middle shell (in elastomers with more than a two-shell structure); with multi-shell elastomers, several shells can also consist of a rubber phase.

If, aside from the rubber phase, one or more hard components (with glass transition temperatures of more than 20°C [68°F]) are involved in the structure of the elastomer, then these are generally produced by means of the polymerization of styrene, acrylonitrile, methacrylonitrile, α -methylstyrene, p-methylstyrene, acrylic acid esters and methacrylic acid esters such as methylacrylate, ethylacrylate and methylmethacrylate as the main monomers. In addition, small portions of other comonomers can also be used here.

In a few cases, it has proven to be advantageous to use emulsion polymers that have reactive groups on the surface. Such groups are, for example, epoxy, amino or amide groups as well as functional groups that can be introduced by also using monomers having the general formula



whereby the substituents can have the following meaning:

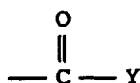
R^{15} is hydrogen or a C_1 - C_4 alkyl group,

R^{16} is hydrogen, a C_1 - C_8 -alkyl group or an aryl group, especially phenyl,

R^{17} is hydrogen, a C_1 - C_{10} -alkyl group, a C_6 - C_{12} -aryl group or $-OR^{18}$

R^{18} is a C_1 - C_8 -alkyl group or a C_6 - C_{12} -aryl group, which can be optionally substituted with groups containing O or N,

x is a chemical compound, a C_1 - C_{10} -alkylene group or a C_6 - C_{12} -arylene group or



V is O-Z- or NH-Z and

Z is a C_1 - C_{10} -alkylene group or a C_6 - C_{12} -arylene group.

The graft monomers described in EP-A 208 187 are suitable for the introduction of reactive groups on the surface.

As additional examples, mention should also be made of acrylamide, methacrylamide and substituted esters of acrylic acid or methacrylic acid such as (N-t-butylamino) ethylmethacrylate, (N,N-dimethylamino)ethylacrylate, (N,N-dimethylamino)methethylacrylate, (N,N-diethylamino)ethylacrylate.

Moreover, the particles of the rubber phase can also be cross-linked. Monomers with a cross-linking effect are, for example, buta-1,3-diene, divinylbenzene, diallylphthalate and dihydrodicyclopentadienylacrylate as well as the compounds described in EP-A 50 265.

Moreover, so-called graft-linking monomers can also be used, that is to say, monomers with two or more polymerizable double bonds that react at different rates during the polymerization. Preferably, such compounds are used in which at least one reactive group polymerizes at about the same rate as the other monomers, whereas the other reactive group (or reactive groups), for example, polymerizes much more slowly. The different polymerization rates entail a certain portion of unsaturated double bonds in the rubber. If another phase is subsequently grafted onto such a rubber, then the double bonds present in the rubber react at least partially with the graft monomers while forming chemical bonds, that is to say, the grafted phase is at least partially cross-linked to the graft substrate via chemical bonds.

Examples of such graft-linking monomers are monomers containing allyl groups, especially allylesters of ethylenically unsaturated carboxylic acids such as allylacrylate, allylmethacrylate, diallylmaleate, diallylfumarate, diallylitaconate or the corresponding monoallyl compounds of these dicarboxylic acids. In addition, there are numerous other suitable graft-linking monomers; for further details, see, for example, U.S. Pat. No. 4,148,846.

In general, the proportion of these cross-linking monomers in component E) amounts to 5% by weight, preferably not more than 3% by weight, relative to E).

A few preferred emulsion polymers are listed below. First of all, mention should be made of graft polymers with a core and at least one outer shell, which have the following structure:

Monomers for the core	Monomers for the shell
buta-1,3-diene, isoprene, n-butylacrylate, ethylhexylacrylate or mixtures thereof, optionally together with cross-linking monomers	styrene, acrylonitrile, (meth)acrylates, optionally with reactive groups as described herein

Instead of graft polymers with a single-shell structure, it is also possible to use homogeneous, that is to say, single-shell elastomers made of buta-1,3-diene, isoprene and n-butylacrylate or their copolymers. These products, too, can be produced by using cross-linking monomers or else monomers with reactive groups.

The elastomers E) described can also be produced by means of other conventional methods, e.g. by means of suspension polymerization.

Other preferred rubbers are polyurethanes like those described in EP-A 115 846, EP-A 115 847, EP-A 116 456, EP-A 117 664 and EP-A 327 384. Such products are commercially available, for example, under the designation Desmopan® (Bayer AG) or Elastollan® (Elastogran Polyurethane GmbH).

Of course, it is also possible to use mixtures of the rubber types listed above.

As component F), the molding compounds according to the invention can contain 0% to 50% by weight, preferably 5% to 40% by weight, of a fibrous or particulate filler or mixtures thereof.

Examples of fillers with a reinforcing effect are potassium titanate whiskers, carbon fibers and preferably glass fibers, whereby the glass fibers can be used, for example, in the form of glass fabrics, glass mats, glass webs and/or glass silk rovings or cut glass silk made of low-alkali E-glass (alkali-free glass) with a diameter ranging from 5 μm to 200 μm , preferably 8 μm to 50 μm , whereby the fibrous fillers preferably have a mean length of 0.05 mm to 1 mm, especially 0.1 mm to 0.5 mm, after they have been processed.

Other suitable fillers are, for example, wollastonite, calcium carbonate, glass beads, quartz powder, silicon nitride and boron nitride or mixtures of these fillers.

Additional commonly used additives and processing auxiliaries are additives to capture formaldehyde (formaldehyde scavengers), plasticizers, lubricants, mold-release agents, adhesives and pigments.

In general, the percentage of such additives lies in the range from 0.001% to 5% by weight.

The molding compounds according to the invention are produced by mixing the components in a generally known manner, which is why detailed explanations are not necessary here. Advantageously, the components are mixed using an extruder.

Subsequently, molded parts are made using conventional, for example, injection-molding, methods, and these parts can be electrostatically coated by means of known methods, for example, Glasurit-Handbuch: Lacke und Farben [Glasurit Handbook: Coatings and Paints], 11th edition, published by Curt-Vincentz-Verlag, Hannover, Germany 1984, pp. 358-371 or K.-A. van Oeteren, Korrosionsschutz durch Beschichtungsstoffe [Corrosion protection by means of coating materials], Volume 2, published by Carl-Hanser-Verlag Munich 1980, pp. 1366-1371. The molded parts also stand out for their good mechanical properties (especially a high modulus of elasticity) and good resistance to fuels and chemicals.

Therefore, such molded parts are very well suited as car body or exterior parts for automotive construction such as panels, parts for exterior mirrors and door handles as well as hatchback handles.

EP 0 831 116 A1

Examples:

The following components were used:

Component A)

Polyoxymethylene copolymer made of 95% by weight of trioxane and 5% by weight of butane diol formal. The product also contained about 3% by weight of unreacted trioxane and 5% by weight of thermally unstable fractions. After the breakdown of the thermally unstable fractions, the copolymer had a melt flow index of 25 ml/10 min at 190°C [374°F] and 2.16 N, according to ISO 1133.

Component B)

Carbon black with a specific surface area according to BET (according to DIN 66 132 of 950 m²/g, a DBP adsorption according to DIN 53 601 of 380 mg/g and an iodine adsorption according to DIN 53 582 of 1075 mg/g.
(Printex® XE2, made by Degussa AG).

Component C)

Sodium hydroxide (metered in as a 50% by weight aqueous solution)

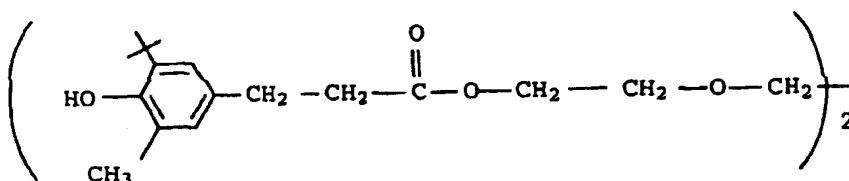
Component D)

Polyamide with a molecular weight of 3000, produced from 37% by weight of ϵ -caprolactam, 63% by weight of an equimolar mixture of adipic acid and hexamethylene diamine, using propionic acid as the regulator.

Component E)

EP 0 831 116 A1

E/1: Irganox® 245 (Ciba-Geigy AG):



E/2: Synthetic MG-silicate (Ambosol® made by Soci t  Nobel, Bozel, Puteaux, France) having the following properties

Content of MgO:	≥ 14.8% by weight
Content of SiO ₂ :	≥ 59% by weight
Ratio of SiO ₂ : MgO	2.7 mol/mol
Bulk density:	20 g to 30 g / 100 ml
Annealing loss:	< 25% by weight

E/3: Melamine formaldehyde condensate used according to Example 1 of DE-A 25 40 207.

In order to produce the molding compounds, component A) was mixed with the amounts of component D) and E) indicated in Table 1 in a dry mixer at a temperature of 23°C [73.4°F]. The mixture thus obtained was placed into a twin-screw extruder with a degassing device (ZSK 28 made by the Werner & Pfleiderer company), at 230°C [446°F] and homogenized, components B) and C) (as a 50% aqueous solution) were metered in together, degassed and the homogenized mixture was extruded through a die as a strand and granulated.

Using an injection-molding machine, test specimens were made at a melt temperature of 200°C [392°F] and a tool temperature of 80°C [176°F]. The modulus of elasticity was

EP 0 831 116 A1

determined according to DIN 53 457 (or ISO 527/2). The volume resistivity DGW [$\Omega \cdot \text{cm}$] was determined according to IEC 93. The surface resistance OFW [Ω] was determined according to IEC 93 with fluid silver electrodes (electrode geometry: 50 mm \times 5 mm, grounded counter-electrode).

The electrostatic coating was carried out at a potential of 90 KV. A basecoat (FE 70) made by BASF Lacke und Farben was used as the coating.

The results of the measurements and the composition of the molding compounds can be found in the tables.

Patent Claims

1. The use of thermoplastic molding compounds made of
 - A) 30% to 94% by weight of a polyoxymethylene homopolymer or polyoxymethylene copolymer,
 - B) 6% to 10% by weight of carbon black with a pore volume (DBP adsorption) according to DIN 53 601 of at least 350 ml/100 grams
 - C) 0% to 2% by weight of an alkali or earth alkali compound or mixtures thereof
 - D) 0% to 2% by weight of a polyamide
 - E) 0% to 60% by weight of further additives and processing auxiliaries.whereby the percentages by weight of components A) through E) add up to 100%, for the production of electrostatically coatable molded parts.
2. The use according to Claim 1, characterized in that the carbon black B) has a specific surface area according to BET (according to DIN 60 132) of at least 900 m²/g.
3. The use according to Claims 1 or 2, characterized in that the carbon black B) has an iodine adsorption (according to DIN 53 582) of at least 950 m²/g.

4. The use according to Claims 1 to 3, characterized in that an alkali hydroxide is used as component C).
5. The use of Claims 1 to 4, characterized in that sodium hydroxide is used as component C).
6. The use according to Claims 1 to 5, characterized in that component D) is used in amounts of 0.001% to 2% by weight.
7. Electrostatically coatable molded parts which can be obtained according to the utilization claims 1 to 6.
8. Electrostatically coatable molded parts according to Claim 7, characterized in that these molded parts are car body or exterior parts for automotive construction.
9. Electrostatically coatable car body or exterior parts according to Claim 8, characterized in that these are panels, hatchback handles, parts for exterior mirrors and door handles.

Translation: Language Solutions
Leonardo and Elise Duvekot
ledtrans@cs.com
November 3, 2004





European
Patent
Office

EUROPEAN SEARCH REPORT

Application Number:
EP 97,157,797

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁶)
X	EP 0,353,932 A (POLYPLASTICS CO.) February 7, 1990 * Claims 1 to 10 *	1 to 9	C08K3/04 C08L59/00
X	EP 0,363,103 A (POLYPLASTICS CO.) April 11, 1990 * Claims 1 to 10 *	1 to 9	
A	US 4,555,357 A (KAUSGA TAKUZO <i>et al.</i>) November 26, 1985		
A	EP 0,453,218 A (ASAHI CHEMICAL IND.) October 23, 1991		
A	DE 28 08 675 A (ASAHI CHEMICAL IND.) September 14, 1978		
A	EP 0,127,084 A (POLYPLASTICS CO.) December 5, 1984		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. ⁶)
			C08K C08L
Place of search: The Hague, The Netherlands		Date of completion of the search: October 21, 1997	Examiner: Stienon, P.
CATEGORY OF CITED DOCUMENTS		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document			